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ABSTRACT

A new extractant for the separation of actinide(III) and lanthanide(III), bis(*o*-trifluoromethylphenyl)phosphinic acid (O-PA) was synthesized. The synthetic route employed mirrors one that was employed to produce the sulfur containing analog bis(*o*-trifluoromethylphenyl)dithiophosphinic acid (S-PA). Multinuclear NMR spectroscopy was used for elementary characterization of the new O-PA derivative. This new O-PA extractant was used to perform Am(III)/Eu(III) separations and the results were directly compared to those obtained in identical separation experiments using S-PA, an extractant that is known to exhibit separation factors of ~100,000 at low pH. The separations data are presented and discussed in terms comparing the nature of the oxygen atom as a donor to that of the sulfur atom in extractants that are otherwise identical.

INTRODUCTION

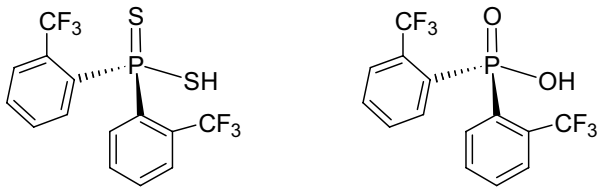
The coordination chemistry and extraction behavior of the actinides(III) and the lanthanides(III) has been extensively examined, yet is still not completely understood. It has been shown that ligands containing hard donor atoms (e.g., O) do not exhibit any selectivity between An(III) from Ln(III) [1]. However, the introduction of softer donor atoms (e.g., S) into similarly structured ligands does offer a differentiation between An(III) and Ln(III) coordination. Exploiting this difference in coordination behavior, various solvent extraction processes have been developed that utilize soft donor atoms to effect the separation of An(III) from Ln(III) [2-8]. However, the incorporation of soft donors alone does not ensure efficient separation of An(III) and Ln(III). A prime example of this is the direct comparison of the commercially available extractant Cyanex-301® (bis-(2,4,4-trimethylpentyl)dithiophosphinic acid) to bis(chlorophenyl)dithiophosphinic acid extractants (see Figure 1). Cyanex is an effective agent for the separation of An(III) from Ln(III) in acidic media, yet the chlorophenyl extractants alone do not show any appreciable lanthanide/actinide selectivity [9-11]. The chlorophenyl extractants only afford appreciable lanthanide/actinide selectivity upon the inclusion of oxygen-bearing organophosphorus synergists, such as trioctylphosphinoxide.

Cyanex 301®

Bis(chlorophenyl)-dithiophosphinic Acid

Figure 1. Example dithiophosphinic acid actinide extractants.

Recently, new aromatic dithiophosphinic acids (R_2PS_2H; S-PA) derivatives were synthesized at the Idaho National Laboratory (INL) [12]. Using the INL extraction process, bis(*o*-trifluoromethylphenyl)dithiophosphinic acid (**1**; Figure 2) efficiently separates Am(III) directly from Eu(III) with separation factors of ~100,000 at low pH [13-14]. In order to better understand this unusually effective separation behavior, the dioxo analog of **1** has been synthesized in our laboratory. In this paper, we describe the synthesis and elementary characterization of the dioxo analog, bis(*o*-trifluoromethylphenyl)phosphinic acid (**2**; Figure 2), and also report a simple comparative extraction study that was conducted between the dithiophosphinic acid, **1** and dioxophosphinic acid, **2**.



(**1**) (**2**)

Figure 2. Bis(*o*-trifluoromethylphenyl)dithiophosphinic acid (**1**) and bis(*o*-trifluoromethylphenyl)phosphinic acid (**2**).

EXPERIMENTAL

Materials and general procedures. All solvents and other reagents were obtained from commercial sources and used as received: sodium hydroxide (Aldrich), anhydrous sodium sulfate (Aldrich), trace metal grade hydrochloric acid (Fisher), anhydrous diethyl ether (Aldrich), anhydrous tetrahydrofuran (Aldrich), anhydrous toluene (Aldrich), and hexanes (Aldrich). Water was purified using a Millipore Nanopure system (purity ~18 MOhms/cm). Proton, $^{19}F\{^1H\}$, $^{31}P\{^1H\}$ and $^{13}C\{^1H\}$ NMR spectra were recorded on a Bruker DMX 300WB spectrometer operating at 7.04 T. Due to adverse interaction with metals, Teflon® or glass had to be used for all manipulations after the final phosphinic acid product was formed.

Synthesis of bis(*o*-trifluoromethylphenyl)phosphinic acid (**2**). The phosphorus(III) reactions (see Scheme 1) followed literature procedures [12]. The final two reaction steps are provided here. Anhydrous toluene (125 mL) was transferred to a 250 mL flask via cannula. $(o\text{-}(CF_3)C_6H_4)_2P\text{-}H$, (8.0 g, 0.025 mol) in anhydrous toluene (25 mL) was slowly added to the flask by syringe. Air was introduced into the flask by a pipette bubbler and the reaction was continuously stirred. This reaction is initially very vigorous (approx. 2 hrs) as the starting phosphine begins to react with oxygen. After this period, the reaction was slowly warmed to a light reflux for 24 hours. At this time, ^{31}P NMR analysis showed ~50/50 mixture of $(o\text{-}(CF_3)C_6H_4)_2POH$ and $(o\text{-}(CF_3)C_6H_4)_2PO_2H$, with trace quantities of the starting phosphine. The toluene was removed at reduced pressure and the solids transferred to another 250 mL flask.

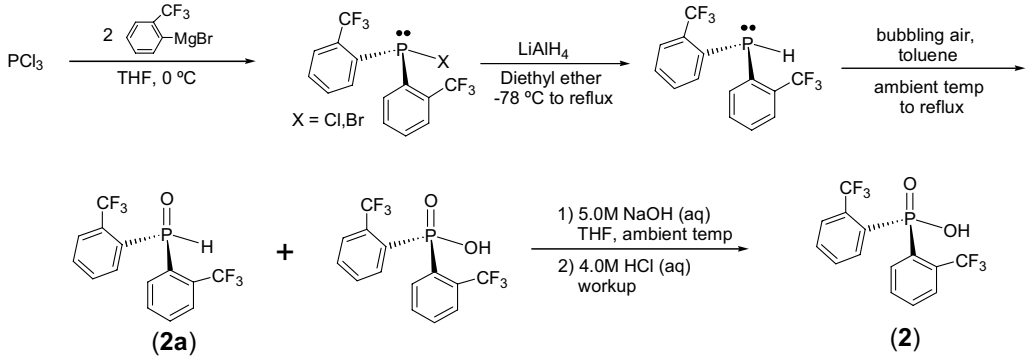
THF (150 mL) was employed to dissolve the solids and an aqueous solution of sodium hydroxide (50 mL; 5.0 M NaOH) was added to the flask. This reaction mixture was vigorously stirred at ambient temperature for 48 hrs, and the organic layer took on a slight red-orange color. The organic and aqueous phases spontaneously separate when stirring is stopped. Using a 250 mL separatory funnel, the organic phase was separated, retained, and then removed at reduced pressure leaving an off-white solid. This solid was dissolved in diethyl ether (125 mL), placed in

a 250 mL separatory funnel, and acidified by shaking with 4.0 M hydrochloric acid (75 mL). The organic layer was collected and the aqueous layer was washed twice with diethyl ether (25 mL). The ether extracts were combined, dried over anhydrous Na_2SO_4, and the ether was removed at reduced pressure. The solid product was recrystallized from diethyl ether/THF and gave prismatic crystals of the product, **2**. Crystals were obtained in 25% yield; mp = 96-97 °C.

Am(III)/Eu(III) separations experiments. Distribution ratios for ^{241}Am and $^{152,\ 154}$Eu (D_M = $[M]_{org}$ / $[M]_{aq}$) are measured by equilibrium batch contacts between the organic and aqueous phases at an organic-to-aqueous phase ratio of unity (O/A = 1). In all experiments, the organic phase is pre-equilibrated by contacting three times with fresh aqueous solution containing the appropriate concentrations of HNO_3 and $NaNO_3$. Thus insures that all components are present at equilibrium concentrations in the organic phase. In all radioactive experiments, the aqueous phase is of the appropriate HNO_3 and $NaNO_3$ concentrations spiked with the radionuclides of interest (^{241}Am and $^{152,\ 154}$Eu) in trace quantities (typically, less than 10^{-7} M each). The phases are mixed by vortex for two minutes to ensure equilibrium is attained and are separated by centrifugation. Each separated phase is sampled and the ^{241}Am and $^{152,\ 154}$Eu activity determined using gamma spectroscopy. A calibrated pH meter was used to experimentally determine the pcH of the aqueous phase after each extraction experiment.

DISCUSSION

Synthesis of the extractants. There are numerous synthetic pathways that can be used for making phosphinic acids (R_2PO_2H; O-PA). The syntheses of O-PAs are well-known, and many different types of O-PAs are commonly used in liquid-liquid extractions for the separation of a wide variety of metals [1-2, 15-16]. The synthetic approach employed to synthesize our O-PA product mirrored our previously developed pathway to the dithiophosphinic acid analog, **1** (Figure 2) [12]. The synthetic route requires four steps to produce the final product. The first step employs a phosphorus(III) halide precursor and attaches the desired organic substituents via selective nucleophilic addition through the use of the corresponding organic Grignard reagents (see Scheme 1).

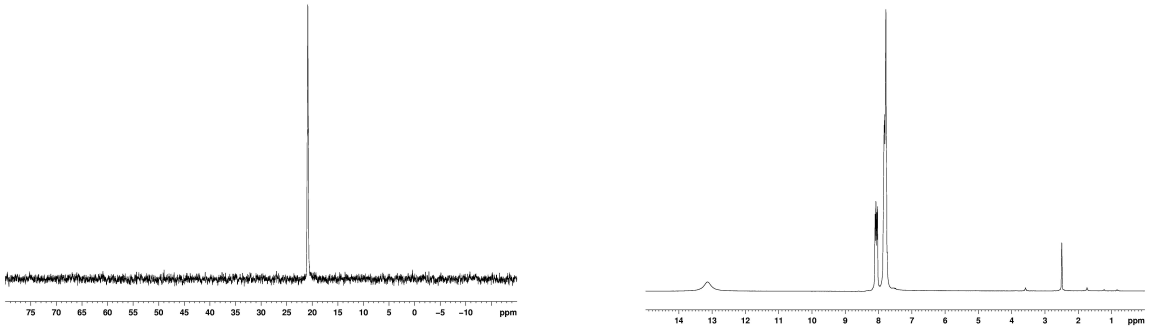


Scheme 1. General synthesis for bis(*o*-trifluoromethylphenyl)phosphinic acid (O-PA; **2**).

Grignard reagents were chosen to perform this coupling reaction because, unlike previous routes to di-functional phosphinic acids [9-11], this methodology affords total control over the regiochemistry of the organic substituents at the phosphorus center, yielding only the desired product instead of a mix of isomers.

The second step in the synthesis uses a strong reducing agent, $LiAlH_4$, to convert the bis(*o*-trifluoromethylphenyl)phosphorus(III) halide into the corresponding di-functional phosphine. These first two steps in this route are identical to that proven in our labs for the production of bis(*o*-trifluoromethylphenyl)dithiophosphinic acid (**1**). However, the oxidation of bis(*o*-trifluoromethylphenyl)phosphine (P-H) to a phosphorus(V) center had not been investigated using oxygen, only elemental sulfur. Initial attempts at converting the phosphine intermediate into the desired O-PA derivative involved the simple exposure of a THF solution of the phosphine to oxygen from the atmosphere. This was found to be ineffective, with only partial oxidation of the phosphine being observed. The reaction is initially vigorous upon the exposure to oxygen from the atmosphere indicating that the first oxygen is rapidly added, yielding compound **2a**. However, the reaction never reached completion, but instead stalled with a nearly 50/50 mixture of **2a** and **2**. Even heating the reaction mixture to reflux while bubbling a stream of air through the solution for two days did not complete the oxidation reaction.

In order to force the conversion of **2a** to the desired O-PA **2**, an aqueous solution of concentrated sodium hydroxide was used. The base solution was added to the THF at ambient temperature, and the reaction was allowed to proceed for two days. Due to the high ionic strength of the aqueous phase, two phases resulted in the absence of vigorous stirring. This strategy was successful as nearly quantitative conversion to the desired product was observed by ^{31}P NMR. All products were in the organic phase as there were no detectable phosphorus compounds in the aqueous phase.



(a) (b)

Figure 3. (a) ^{31}P NMR; (b) ^{1}H NMR of (*o*-$(CF_3)C_6H_4)_2PO_2H$), **2,** in DMSO-d_6.

The oxidized product was isolated by stripping off the THF solvent to yield a white solid, the sodium salt of **2**. Dissolving this solid into a suitable organic solvent and acidifying with hydrochloric acid afforded the final crude product. To further purify the product, it was recrystallized once from diethyl ether/THF to give colorless, transparent, prismatic crystals. While this recrystalization did afford **2** in high purity, the yield for this step was surprisingly low, bringing the overall yield down to 25% based on starting phosphorus halide. Characterization of these crystals was accomplished through multinuclear NMR analysis, see Figure 3. The ^{31}P NMR spectrum of **2** consisted of a singlet at 20.7 ppm and showed no coupling between the phosphorus and fluorine, as was expected since this coupling was also absent the sulfur analog, **1**. The ^{1}H NMR spectrum of **2** exhibited a resonance at 13.2 ppm, assigned to the acid proton, as well as exhibiting the expected aromatic envelope.

Extraction behavior of the O-PA (**2**) and S-PA (**1**) towards Ln(III) and An(III). The most interesting behavior of S-PA is the actinide/lanthanide separation efficiencies as evidenced through Am(III)/Eu(III) separations [13,14]. The results obtained indicate that **1** exhibits orders-of-magnitude better performance in terms of the separation efficiency compared to currently available actinide/lanthanide selective extractants. When dissolved in a suitable organic diluent, in this case trifluoromethylphenyl sulfone, (FS-13) **1** is able to separate Am(III) from Eu(III) in acidic aqueous solutions with separation factors (S_{Eu}^{Am}) of ~100,000 at low pH, indicating that an extremely efficient process for the separation of trivalent actinides from trivalent lanthanides could be realized. However, the reason for this separation ability remains poorly understood. To shed some light on the coordination chemistry of **1**, an analog that is structurally identical, yet possesses oxygen donor atoms in place of sulfur atoms was desired, hence this work was undertaken. Once the new extractant (**2**) was synthesized, it was evaluated side-by-side with **1**. The distribution ratios for the partitioning of Am(III) and Eu(III) between a 0.1 M solution of **1** or **2** in FS-13 solvent and the original aqueous phase as a function of pcH are shown in Figure 4. In all cases the aqueous phase contained 1.0 M total NO_3^-, where the acidity is set for each experiment and the balance of cations are Na^+. The pcH was determined after each extraction.

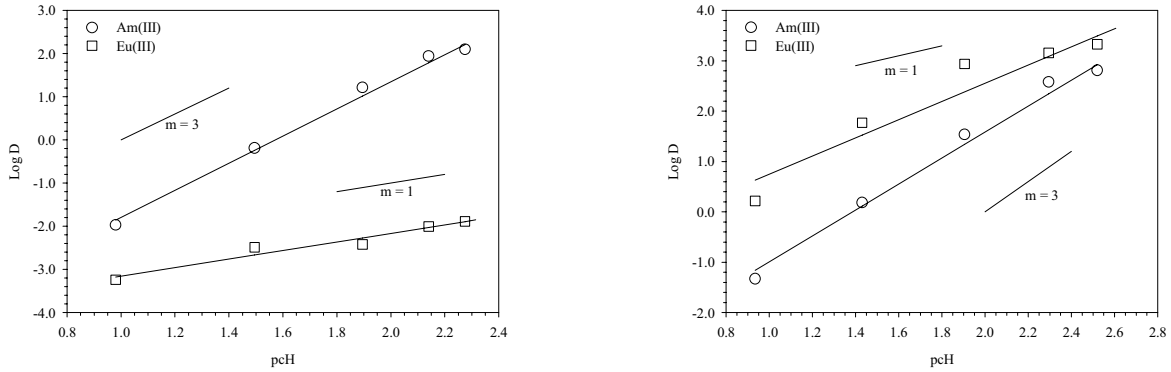


Figure 4. Extraction of Am(III) and Eu(III) in FS-13 by **1**(left) and **2**(right) as a function of pcH.

The positive slope (m ~ 3) of the Am extraction acid dependence of **1** is consistent with an acidic, cation-exchange extraction mechanism in which three protons are exchanged to the aqueous phase for each Am complex formed in the organic phase. The significantly different slope (m ~ 1) in the case of the Eu extraction acid dependence of **1** suggests the Eu complex has a dramatically different stoichiometry which may be indicative of a fundamentally different interaction mode between this extractant and Eu. The slopes of the acid dependencies for the extraction of Am (m ~ 3) and Eu (m ~ 1) by **2** are quite similar to those observed for **1**, which indicates that the mode of extractant/metal interactions are likewise similar between the two extractants, as expected given the similarity in structure between **1** and **2**. The separation factors ($S_{Eu}^{Am} = D_{Am}/D_{Eu}$) observed for **1** demonstrate that this ligand is able to selectively extract Am(III) in the presence of Eu(III). However, in the case of **2**, the Am/Eu selectivity is reversed with separation factors of only $S_{Am}^{Eu} = 10$. Based on these observations, the replacement of the softer sulfur donors with oxygen donors with otherwise identical extractant architecture does lead to a decrease in actinide/lanthanide selectivity. This is principally due to the ability of the harder oxygen donors to effectively remove the Eu from the aqueous phase, (all Eu distributions observed were >1) whereas the softer sulfur donors are unable to effect this phase transfer (all Eu distributions observed were <<1).

CONCLUSIONS

In this work, two extractants that were identical in all structural aspects except for the nature of the donor atoms (S vs. O) were synthesized and their extraction behavior directly compared. The synthesis of **1** was reported previously, but the details for the synthesis of **2** were first presented in this work. The route chosen to produce **2** closely followed the route found to be successful for **1**. However, for **2**, oxidation of the trivalent phosphine intermediate to the corresponding end product was not as successful as found for **1**. While this method was successful in producing purified **2**, alternate routes are under investigation in our labs that will produce the desired O-PA derivatives in better yields. The extraction behavior for **1** and **2** were found to be quite different, yet the mechanisms of metal extraction were found to be similar as expected between **1** and **2**. The extractant:Am interaction was found to be consistent with acidic, cation-exchange extraction mechanism, and the extractant:Eu interaction was found to be quite different and is less well understood. **1**, by virtue of its high separation factor ($S_{Eu}^{Am} \sim 100{,}000$) is amenable to the direct extraction of Am from aqueous acidic solutions of Am and Eu. However, by the judicious choice of aqueous phase acidity, a separation of Eu(III) from Am(III) using **2** could also be accomplished.

ACKNOWLEDGMENTS

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